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PATENT SPECIFICATION

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(54) A PROCESS FOR THE PRODUCTION OF ALKENES

(71) We, SHELL INTERNATIONAL-
 ALE RESEARCH MAATSCHAPPIJ B.V.,
 a company organized under the laws of the
 Netherlands, of 30 Carel van Bylandtlaan,
 The Hague, The Netherlands, do hereby
 declare the invention, for which we pray that
 a patent may be granted to us, and the method
 by which it is to be performed, to be particu-
 larly described in and by the following state-
 ment:—

The present invention is concerned with a
 process for the production of an alkene with
 at least 6 carbon atoms per molecule or a
 mixture of such alkenes starting from a mix-
 ture of predominantly non-terminal alkenes.

In US Patent Specification No. 3,726,938
 an integrated process for the production of
 alkenes is described in which a disproportiona-
 tion step is involved, preceded by an oligo-
 merization and an isomerization step. The
 feed to the disproportionation zone predomi-
 nantly consists of non-terminal olefins. It is
 mentioned that the effluent from the dispropor-
 tionation zone is separated into a lower olefin
 fraction, an intermediate olefin fraction, which
 is recovered as product, and a higher olefin
 fraction. The lower and the higher olefin frac-
 tions may be recycled to upstream sections
 of the process, e.g. to the oligomerization and/
 or the isomerization zone.

It has now been found that it is often
 advantageous instead of isolating the desired
 alkene(s) directly from the effluent of the dis-
 proportionation zone to subject said effluent
 to isomerization followed by a further dispropor-
 tionation in the presence of one or more
 non-terminal alkenes with a larger number of
 carbon atoms than said desired alkene(s).
 Without the necessity of installing extensive
 and costly extra separation equipment, in par-
 ticular extra distillation columns, and without
 having to recycle large streams of non-con-
 verted or unwanted alkenes, the yield in which
 the desired alkene(s) is (are) obtained is
 usually increased significantly.

According to the present invention there is
 provided a process for the production of an
 alkene with at least 6 carbon atoms per mole-

cule or a mixture of such alkenes, which com-
 prises (1) catalytically disproportionating a
 mixture of predominantly non-terminal alkenes
 which mixture includes a major proportion of
 an alkene or alkenes having a larger number
 of carbon atoms than the alkene(s) to be
 produced and, optionally, an alkene or alkenes
 having a smaller number of carbon atoms than
 said alkene or alkenes, (2) isomerising at least
 part of the resulting disproportionation product,
 which part of said product contains an alkene
 or alkenes with the same number of carbon
 atoms as the alkene with at least 6 carbon
 atoms per molecule or mixture thereof to be
 produced, (3) catalytically disproportionating
 at least part of the resulting isomerisation
 product together with at least one non-terminal
 alkene with a larger number of carbon atoms
 than the alkene with at least 6 carbon atoms
 per molecule or mixture thereof to be pro-
 duced, said at least one non-terminal alkene
 being added to said isomerisation product and/
 or being present therein as a result of being
 present in the disproportionation product of
 stage (1), and (4) removing the desired alkene
 or alkene mixture from the product of stage
 (3).

If desired, any alkene(s) having a smaller
 number of carbon atoms than the alkene with
 at least 6 carbon atoms per molecule or mix-
 ture thereof to be produced which may be
 present in said isomerisation product are re-
 moved therefrom prior to the disproportiona-
 tion thereof in stage (3).

The mixtures of predominantly non-terminal
 alkenes have a content of internal alkenes which
 is at least 50% and preferably at least 70%.
 Recommended feedstocks contain at most 15%
 and preferably less than 10% of α -olefins.
 They may, inter alia, be obtained by dehydro-
 genation of the corresponding alkanes. A very
 suitable starting material is a mixture of pre-
 dominantly non-terminal alkenes with 4 to 60
 carbon atoms per molecule, although mixtures
 containing still higher alkenes e.g. up to C₈₀-
 alkenes, are suitable. It is considered desirable
 that the double-bonds are present at particular
 internal locations in the initial alkenes. De-

pending on the number of carbon atoms of the alkene the preferred location of the double bond can be found at any internal position in the molecule. Favourable feedstocks in this respect can be conveniently obtained, for instance, by oligomerization of ethylene, followed by double-bond isomerization of the oligomerization product, or a fraction thereof. The oligomerization can suitably be performed according to one of the methods known in the art. Very suitable is a process as described in British Patent Specification No. 1,353,873, and the pertinent portions of that reference as regards the reaction conditions and oligomerization catalysts are incorporated in and made part of this specification for the purpose of describing this process in more detail.

Although some branching of the alkenes present in the starting mixtures can be tolerated it is preferred to use mixtures substantially consisting of linear alkenes.

In carrying out the process of the present invention the alkene(s) with at least 6 carbon atoms per molecule can be separated from the product of the disproportionation stage (1) and thereafter isomerised, and, after admixture with one or more non-terminal (i.e. internal) alkenes with a larger number of carbon atoms than the alkene or alkene mixture to be produced, which non-terminal alkenes can be derived from any desired source, subjected to the further disproportionation of stage (3). However, savings are usually obtained, especially as regards separation equipment, if at least part of the total product obtained in the disproportionation stage (1) is directly subject to double-bond isomerization. Accordingly, the latter procedure is generally preferred.

For similar reasons it is preferred to subject the total product obtained in the double-bond isomerisation of stage (2) to the disproportionation treatment stage (3) in admixture with said one or more non-terminal alkenes. It will be understood that small streams, such as heavy materials, can be removed from the process, as so-called bleed streams, between stages (1) and (2) and stages (2) and (3).

According to a preferred embodiment of the present process at least part of the total product obtained from the disproportionation stage (3) is subjected to a further double-bond isomerization and a further disproportionation prior to the removal of the desired alkene or alkene mixture. It has been observed that this frequently results in a still higher yield of the alkene(s) to be produced. If desired, more such sequences, each comprising a double-bond isomerization followed by disproportionation, may be added, but as a rule this will not result in significant further improvements.

The double-bond isomerization of alkenes is old per se in the art and many catalysts are known which have proved satisfactory for

that purpose. In this connection reference made to F. Asinger, "Monoolefins Chemistry and Technology" pages 1020—1104 (English edition 1968), "International Journal of Methods in Synthetic Organic Chemistry", Part I in No. 3 pages 97—112, November, 1969, and Part II pages 405—430, August, 1970, and H. Dunning "Review of Olefin Isomerization", Industrial and Engineering Chemistry 45 (1953), page 551 ff.

In view of their high catalytic activity permitting the use of relatively low isomerization temperatures, supported basic alkali-metal compounds are preferred isomerization catalysts, and among these in particular basic salts of potassium supported on an active alumina such as gamma- or eta alumina. Moreover, the regenerability of these catalysts is good. The use of potassium carbonate supported on gamma-alumina is most preferred. In this connection reference is made to the specification of British Patent Application 33782/73 (Serial No 1392909) and the pertinent portions of that reference as regards the conditions for catalyst activation and isomerization reaction are incorporated in and made part of this specification for the purpose of describing this process in more detail.

The disproportionation of alkenes as used in the process according to the invention has likewise been described in various publications. Besides US Patent Specification 3,726,938 already mentioned above, reference is made to a review article by G. C. Bailey in "Catalytic Reviews" 3 (1), pages 37—60 (1969).

Recommended catalysts include supported molybdenum oxide, tungsten oxide supported on silica and rhenium heptoxide supported on alumina. The use of rhenium oxide-containing catalysts is not always satisfactory since these catalysts, unless applied at very low temperatures, also promote the formation of skeleton isomers. This phenomenon is not or hardly observed when molybdenum oxide-containing catalysts are applied. Moreover in the presence of the latter catalysts, also the disproportionation of the higher alkenes, e.g. those having more than 25 carbon atoms per molecule, proceeds at high rate. Most preferred is a catalyst system comprising molybdenum oxide, promoted by cobalt oxide, on an aluminium oxide support.

In order to ensure an easy recovery of the various process streams it is generally recommended to use solid catalysts, albeit that in the final disproportionation treatment application of a homogeneous catalyst might be considered.

An advantage of the process according to the invention is that, by a proper selection of the catalysts, in the double-bond isomerization and disproportionation treatments the same or substantially the same reaction temperatures may be applied so that no intermediate heating or cooling is required. With

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potassium carbonate on alumina as isomerization catalyst and molybdenum oxide/cobalt oxide/alumina as disproportionation catalyst preferred reaction temperatures are in the range 60 to 250°C. An additional advantage inherent in the use of these catalysts is that their activation can be performed under identical or nearly identical conditions. Very favourable is an activation, performed in the presence of nitrogen at temperatures in the range 350 to 700°C, in particular between 500 and 600°C.

The double-bond isomerization and disproportionation stages may be carried out with the use of fluidized or fixed bed catalysts. The fixed beds may be operated at any desired mutual distance. However, it is preferred that no actual admixture of isomerization and disproportionation catalysts takes place, since this would adversely affect the flexibility of the process e.g. replacement of deactivated catalyst material. According to a preferred embodiment of the process consecutive double-bond isomerisation and disproportionation stages are performed in at least two contiguous fixed beds of catalyst providing, respectively, for said isomerisation and disproportionation.

From the product obtained in the final disproportionation stage one or more alkene fractions may be recovered, preferably in the C_6 — C_{20} range. Depending on the initial feedstock and the prevailing process conditions, the formation of alkenes in a particular range is facilitated, e.g. in the C_8 — C_{12} , C_{10} — C_{14} or C_{14} — C_{18} range.

The production of alkenes in the C_{11} — C_{14} range is especially favoured, mainly because of their importance as starting material for biodegradable synthetic detergents, chemical and light-resistant alkyl resins and other products. The higher alkenes in the C_{14} — C_{20} range are also useful for the preparation of lubricating oil additives.

The process of the present invention is further illustrated by the following Examples, in which Example III is included for comparative purposes:

EXAMPLE I.

In order to demonstrate the effect achieved by the process according to the invention, an experiment was performed in which C_{11} — C_{14} alkenes were produced starting from a feed-

stock consisting of admixed n-octene and n-eicosene. It will be understood that normally the feedstocks utilized in commercial practice will be of a more complex nature.

The isomerization catalyst was prepared as follows: Gamma-alumina (spec. surface area 350 m²/g, pore volume 0.42 ml/g) in the form of 0.5—1.0 mm spheres was heated in air at 500°C for 2 hours and then mixed with a measured amount of an aqueous solution of potassium carbonate, sufficient to fill the pores of the alumina with liquid. The alumina thus impregnated was dried in air for 3 hours at 120°C. and at 0.033 bar abs. After activation the catalyst contained 3.6 milligram atoms K per gram of alumina and, calculated on total composition, 0.7%w of sodium compounds calculated as Na₂O, 0.02%w of silicon compounds, calculated as SiO₂ and 0.025%w of iron compounds, calculated as Fe₂O₃.

A commercially available disproportionation catalyst was applied (spec. surface area 255 m²/g, pore volume 0.54 ml/g, bulk density 0.52 g/cm³), consisting of cylindrical extrudates (diameter 1.6 mm, length 4.8 mm). Its composition was, calculated on alumina: 15.7%w MoO₃, 3.0%w CoO, 0.37%w sulphur compounds calculated as sulphate and 0.02%w sodium compounds, calculated as Na₂O.

Both catalysts were activated for 16 hours at 575°C in a stream of nitrogen (2.7 l h⁻¹ g⁻¹ catalyst).

The feed, an initial mixture of 1-octene and 1-eicosene (molar ratio 4:1), was introduced into a cylindrical tube with a diameter of 1 cm which contained four contiguous fixed beds, the first and third being isomerization beds, the second and the fourth being disproportionation beds, taken in the flow direction. Each bed contained 4 grams of catalyst. In the first bed the 1-alkenes were isomerized into a mixture of non-terminal octenes and eicosenes, which mixture was subjected to disproportionation in the second bed. The product mixture now containing, inter alia, C_{11} — C_{14} alkenes was subjected to double-bond isomerization in the third fixed bed and subsequently, in the fourth bed, to a second disproportionation. From the effluent thus obtained the C_{11} — C_{14} fraction was recovered.

Results and further reaction conditions are given in the following Table:

TABLE

Example	Weight hourly space velocity, kg.kg ⁻¹ .h ⁻¹ a)	Reaction temp. °C	Total amounts of catalyst, g I(som.) D(ispr.)	Product analyzed at run hour	Conversion %w b)	Yield of C ₁₁ -C ₁₄ %w	Content of C ₂₁ + %w
I	2.6	125	8	8	88.4	22.8	17.3
II	4.1	125	8	8	87.2	22.0	16.7
III	4.4	125	10	5	88.4	20.6	20.7
(for com- parison only)	2.7	125	8	8	83.6	19.4	15.6
a) based on total catalyst	3.9	125	8	8	82.9	18.7	15.4

b) 100%w - (%w C₈ + %w C₂₀ in product)

EXAMPLE II.

Similarly another experiment was carried out, the difference being that the cylindrical reactor tube was provided with 12 contiguous fixed beds, the first of which contained 2 grams of isomerization catalyst, the 3rd, 5th, 7th, 9th and 11th bed each contained 1.6 gram of isomerization catalyst, and the 2nd, 4th, 6th, 8th, 10th and 12th bed each contained 0.83 gram of disproportionation catalyst. Further conditions and the results are given in the above Table. It is noteworthy that since the indicated space velocity is based

on total catalyst, in this experiment very high space velocities per bed were applied.

EXAMPLE III (for comparison only).

A further experiment was performed in which the reactor tube was provided with a single isomerization bed and a single contiguous disproportionation bed. From this disproportionation bed a C₁₁-C₁₄ containing product was obtained which was analyzed. Hence in this experiment no rearrangement took place of double bonds in the C₁₁-C₁₄ portion of the product from the first dispro-

portionation treatment and no second disproportionation was performed. The results are included in the above Table.

WHAT WE CLAIM IS:—

1. A process for the production of an alkene with at least 6 carbon atoms per molecule or a mixture of such alkenes, which comprises (1) catalytically disproportionating a mixture of predominantly non-terminal alkenes which mixture includes a major proportion of an alkene or alkenes having a larger number of carbon atoms than the alkene(s) to be produced and, optionally, an alkene or alkenes having a smaller number of carbon atoms than said alkene or alkenes, (2) isomerising at least part of the resulting disproportionation product, which part of said product contains an alkene or alkenes with the same number of carbon atoms as the alkene with at least 6 carbon atoms per molecule or mixture thereof to be produced, (3) catalytically disproportionating at least part of the resulting isomerisation product together with at least one non-terminal alkene with a larger number of carbon atoms than the alkene with at least 6 carbon atoms per molecule or mixture thereof to be produced, said at least one non-terminal alkene being added to said isomerization product and/or being present therein as a result of being present in the disproportionation product of stage (1), and (4) removing the desired alkene or alkene mixture from the product of stage (3).
2. A process as claimed in claim 1, in which any alkene(s) having a smaller number of carbon atoms than the alkene with at least 6 carbon atoms per molecule or mixture thereof to be produced which may be present in said isomerisation product are removed therefrom prior to the disproportionation thereof in stage (3).
3. A process as claimed in claim 1 or claim 2, in which a mixture of predominantly non-terminal C_4 — C_{10} alkenes is fed to stage (1).
4. A process as claimed in any one of claims 1 to 3, in which a mixture of alkenes obtained by oligomerization of ethylene followed by double bond isomerization of the oligomerization product or a fraction thereof is fed to stage (1).
5. A process as claimed in any one of claims 1—4, in which the total product ob-

tained in the disproportionation stage (1) is fed to said isomerization stage (2).

6. A process as claimed in any one of claims 1—5, in which at least part of the total product from the disproportionation stage (3) is subjected to a further double-bond isomerization and a further disproportionation prior to the removal of the desired alkene or alkene mixture.

7. A process as claimed in any one of claims 1—6, in which one or more alkene fractions in the C_6 — C_{20} range are recovered from the product from the last disproportionation.

8. A process as claimed in claim 7, in which C_{11} — C_{14} alkene fraction is so recovered.

9. A process as claimed in any one of claims 1—8, in which the disproportionation catalyst comprises an oxide of molybdenum and of cobalt, supported on alumina.

10. A process as claimed in any of claims 1—9, in which the isomerization catalyst comprises a basic salt of potassium supported on active alumina.

11. A process as claimed in any one of claims 1—10, in which the isomerization and/or disproportionation catalysts have been activated by a heat treatment in the presence of nitrogen.

12. A process as claimed in any one of claims 1—11, in which consecutive isomerization and disproportionation stages are effected in at least two contiguous fixed beds of catalyst providing respectively for double-bond isomerization and disproportionation.

13. A process as claimed in any one of claims 9—12, in which said double-bond isomerization(s) and said disproportionations are performed at a temperature in the range 60 to 250°C.

14. A process for the production of an alkene with at least 6 carbon atoms per molecule or a mixture thereof substantially as hereinbefore described with reference to Example I or Example II.

15. An alkenes with at least 6 carbon atoms per molecule or a mixture thereof prepared by the process claimed in any one of claims 1—14.

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